

PATENT SPECIFICATION

(11) 1 427 832

1 427 832

- (21) Application No. 31154/73 (22) Filed 29 June 1973
 (31) Convention Application No. 65020/72
 (32) Filed 30 June 1972 in
 (33) Japan (JA)
 (44) Complete Specification published 10 March 1976
 (51) INT CL² C08F 8/34
 (52) Index at acceptance
 C3P D9A10 D9A1 D9A4 D9B10 D9B4X D9D7D2



(54) CROSS-LINKED, FILAMENTARY, METAL CHELATING RESINS

(71) We, TEIJIN LIMITED, a Japanese body corporate, of No. 1, Umeda, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a metal-chelating, solvent-resistant filamentary structure having superior metal-chelating ability characterized by high metal-chelating velocity and chelating capacity for various metal ions, insolubility in boiling toluene, uniformity of crosslinkages, and good durability under conditions required for regeneration treatment, and to a process for its production within a shortened cross-linking time.

By the term "filamentary structure" is meant firstly a filament, secondly a thread-like element made from filaments such as a fiber, yarn, tow or strand and thirdly a shaped structure made from such filaments or thread-like elements such as a web, mat, knitted fabric, woven fabric or non-woven fabric.

Metal-chelating resins in the form of filamentary structures have recently attracted attention because of their superior metal-chelating velocity and ease of separation from the treating liquid compared with those in the granular form. Furthermore, the metal-chelating resins when used as a filtering material allow filtration and capture of metallic ions simultaneously. Also metal-chelating resins in the form of a belt make it possible to capture metallic ions continuously from the treating liquid.

A granular metal-chelating resin made by chloromethylating and iminodiacetylating granules of polystyrene cross-linked with divinyl benzene, and a granular metal-chelating resin obtained by reacting the above chloromethylated granules with a polyethylene-polyamine, have been used. The chelating-forming reaction of these granular metal-chelating resins with metal ions occurs by the infiltration

and diffusion of the metal ions into the resin particles, and therefore the metal-chelating velocity is limited, even in the case of granules of porous polystyrene cross-linked with divinyl benzene, the so-called MR-type granules. The above polystyrene cross-linked with divinyl benzene is stable under severe chemical conditions employed for the introduction of a metal-chelating group, but because it is already in the cross-linked state, it cannot be formed into fibres. On the other hand, the fibers of fiber-forming polymers, such as polyamides, non-cross-linked polystyrene or polyesters, undergo degradation or decomposition under conditions required for introduction of a metal-chelating group, for example, during chloromethylation or sulfonation, thus making it impossible to provide a suitable metal-chelating filamentary structure from the above fiber-forming polymers.

One attempt has previously been made to provide a metal-chelating filamentary structure by utilizing polyvinyl alcohol in the form of a filament. According to this, a polyvinyl alcohol filament was reacted with ethyleneimine to introduce aminoethyl ether groups, and then carboxymethylated to form a metal-chelating filament. However, since this metal-chelating filament has an ether linkage within the molecules, it cannot withstand the regeneration with strong acids required for repeated use. It is also known to react a nylon-6 fiber with a ketone dimer to introduce an acetoacetic acid amide group for the purpose of imparting an antistatic effect. However, the polyamide fiber as a base is very weak to strong acids, and difficult to regenerate and use repeatedly for capturing metal ions.

The present invention provides a metal-chelating, solvent-resistant, filamentary structure (as hereinbefore defined) comprising at least 20% by weight of aromatic nuclear structural units derived from an aromatic monovinyl monomer, which monomer may have a substituent in the ring or a methyl substituent in the α -position, 2 to 40, preferably 5 to 15, per 100 of the aromatic nuclear structural units

50

55

60

65

70

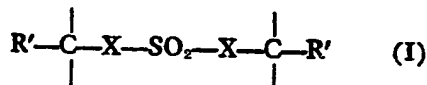
75

80

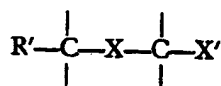
85

90

being cross-linked via an $\text{—SO}_2\text{—}$ group to provide a crosslinked component of the following formula (I)



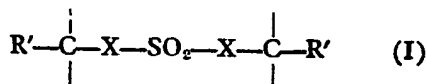
- 5 wherein each X, which may be the same or different, represents one of said aromatic nuclear structural units, and each R', which may be the same or different, represents a hydrogen atom or a methyl group, the fila-
10 mentary structure not containing a cross-linked component of the formula



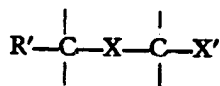
- 15 wherein X' represents —H or X and R' are as defined above, and at least some of the uncrosslinked aromatic nuclear structural units having a metal-chelating group incorporated therein.

- 20 The present invention further provides a method for producing such a filamentary structure which method comprises

- 25 a) reacting a polymeric filamentary structure with chlorosulfonic acid, the polymer comprising at least 20% by weight of aromatic nuclear structural units derived from an aromatic monovinyl monomer, which monomer may have a substituent in the ring or a methyl substituent in the α -
30 position, to form a cross-linked polymeric filamentary structure in which 2 to 40 per 100 of the aromatic nuclear structural units are cross-linked via an $\text{—SO}_2\text{—}$ group to provide cross-linked components of the formula (I)



- 35 wherein each X, which may be the same or different, represents one of said aromatic nuclear structural units and each R', which may be the same or different, represents a hydrogen atom or a methyl group, and
40 which does not contain cross-linked components of the formula



wherein X' represents —H or X and X and R' are as defined above, and

- 45 b) reacting the cross-linked polymeric filamentary structure obtained in step a) with

at least one reagent to introduce a metal-chelating group into at least some of the uncrosslinked aromatic nuclear structural units.

In our copending Application No. 22386/73 (British Patent Specification No. 1,427,831), we describe and claim a filamentary structure comprising aromatic nuclear structural units as defined in this invention. 2 to 40 per 100 of these aromatic nuclear structural units are cross-linked via an SO_2 group, but ion-exchange groups are introduced into at least some of the uncrosslinked aromatic nuclear structural units.

The metal-chelating, solvent-resistant filamentary structure of this invention has various improved properties such as excellent metal-chelating velocity, high chelating capacity for various metal ions especially multi-valent metal ions, insolubility in boiling toluene under atmospheric pressure, uniformity of crosslinkages and good durability under conditions required for regeneration treatment, and can be produced easily within shortened periods of time.

Preferred examples of aromatic monovinyl monomers from which the aromatic nuclear structural units may be derived are styrene, α -methylstyrene, halogenated styrenes, and vinyl naphthalenes. Examples of preferred polymers or copolymers are those comprising homopolymers of units derived from the aromatic monovinyl monomers, especially styrene, copolymers of units derived from at least two of the above aromatic monovinyl monomers, and copolymers of units derived from at least one of the above aromatic monovinyl monomers with units (not more than 80% by weight of the total units) derived from monomers copolymerizable therewith, such as ethylene, propylene, acrylonitrile, methacrylic acid esters or vinyl acetate. Blends of at least two of said polymers or copolymers, or blends of at least one of said polymers or copolymers with other polymers or copolymers can also be used.

In any of the above-mentioned cases, the organic polymer for forming the filamentary structure comprises at least 20% by weight, preferably at least 40% by weight, more preferably at least 65% by weight, of aromatic nuclear structural units derived from an aromatic monovinyl monomer. Where the other polymers or copolymers of the blends as described above are easily soluble in an ordinary solvent such as benzene, toluene, methyl ethyl ketone or methylene chloride, it is recommended that the polymers or copolymers comprising units according to this invention be blended in an amount of at least 40% by weight, preferably at least 65% by weight, more preferably at least 80% by weight, based on the weight of the blend. Where other polymers or copolymers which are sparingly

50

55

60

65

70

75

80

85

90

95

100

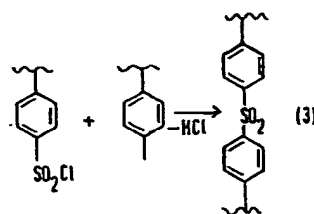
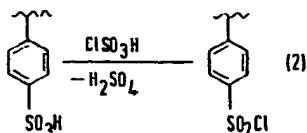
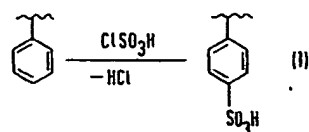
105

110

soluble in the above solvents are used, it is recommended that the polymers or copolymers comprising units according to this invention be blended in an amount of at least 30% by weight, preferably at least 40% by weight, more preferably at least 65% by weight, based on the weight of the blend. The term "filamentary structure" (as hereinbefore defined) may include fibers of optional denier produced by melt-spinning, dry-spinning or wet-spinning the above polymers, copolymers or blends; composite fibers made from such fibers; fibrous materials obtained by forming such polymers, copolymers or blends into films and slitting the films by any desired method, or fibrous materials obtained by extruding the above polymers together with a blowing agent through a die slit and drawing the extruded product in one direction. It may also include filamentary structures produced from these materials by known methods. A fibrous material in the form of non-woven cloth obtained by extruding a polymer containing a foaming agent through a die slit, where the individual constituent fibers of the material are connected in a reticulate fibrous structure is especially preferred. Because of the stretching of the reticulate fibrous structure, this material can be maintained at a constant length even against swelling or shrinkage during a chemical treatment.

According to this invention, the crosslinking reaction can be performed by contacting the filamentary structure with chlorosulfonic acid. The chlorosulfonic acid may be undiluted or diluted with a solvent. When the solvent is a good solvent for the aromatic monovinyl polymer, for example, methylene chloride, chloroform, 1,2-dichloroethane or tetrachloroethane, the concentration of chlorosulfonic acid should be at least 85% by weight, otherwise the form of the filamentary structure cannot be retained. Where the solvent is a nonsolvent for the aromatic monovinyl polymer, for example, sulfuric acid, the concentration of chlorosulfonic acid should be not less than 30% by weight, otherwise the sulfone crosslinkages are not formed to the desired extent.

Taking as an example, polystyrene, this crosslinking insolubilizing reaction can be shown schematically as follows:



The crosslinking reaction consists of the above three stages. If the concentration of chlorosulfonic acid is low, the aromatic ring is consumed by reaction (1) before reaction (2) having a relatively slow rate of reaction proceeds. Therefore, the ratio of crosslinkages to be brought about by reaction (3) decreases. Furthermore, if the reaction temperature is low, reaction (3) proceeds to a greater extent since reaction (1) is more temperature dependent than reaction (3). This may result in excessive crosslinking.

The conditions for the reaction with chlorosulfonic acid may be selected from those which result mainly in the formation of sulfone crosslinkages according to the conditions required for introducing the desired functional group after the crosslinking reaction. It is also possible to choose conditions which will effect sulfone crosslinking and the introduction of chlorosulfonyl groups at the same time, and then to convert the chlorosulfonyl groups to functional groups having metal-chelating ability.

For example, where it is desired to limit the number of the crosslinked components of formula (I) to not more than 10 per 100 of the aromatic nuclear structural units and to introduce about 1 to 30 chlorosulfonyl groups per 100 of said aromatic nuclear structural units, the reaction is preferably carried out at about 25° C. for 1 to 30 seconds. When it is desired to provide about 30 crosslinked components of formula (I) per 100 of the aromatic nuclear structural units and to introduce about 50 to 70 chlorosulfonyl groups, the reaction is preferably carried out at about 25° C. for 3 to 20 minutes. Usually, the reaction temperature is from -20° to +80° C., and the reaction time from 1 second to 30 minutes.

The actual operation of the crosslinking reaction is not particularly restricted, and any desired means can be employed which will ensure uniform contact between the filamentary structure and chlorosulfonic acid. For example, the filamentary structure may be dipped in chlorosulfonic acid, or passed through a chlorosulfonic acid bath, or chlorosulfonic acid may be sprayed onto the filamentary structure.

This contact with chlorosulfonic acid imparts a high level of solvent-resistance to the filamentary structure of the aromatic monovinyl polymer without impairing its original

shape and properties. Since the filamentary structure has a very large surface area as compared with a granular material, the cross-linkages can be formed almost uniformly within the polymer, and only the sulfone group crosslinkage can impart the required solvent-resistance to the filamentary structure.

When granular polystyrene is immersed in 100% chlorosulfonic acid, the resin is partially carbonized and colored. In contrast, a fibrous material of polystyrene can be treated uniformly without carbonization even when immersed in 100% chlorosulfonic acid. This is because the surface area is larger and local heat generation by the reaction is reduced.

The cross-linking treatment of an aromatic monovinyl polymer in this invention can be performed efficiently within very short periods of time. The resulting cross-linked filamentary structure has superior solvent resistance, thermal resistance and chemical resistance and is superior to that obtained by conventional techniques.

Conventional techniques for cross-linking an aromatic monovinyl polymer include a method wherein a copolymer of units derived from an aromatic monovinyl monomer and a polyene or an alkenyl halide is treated with a Lewis acid or strong acid to alkylate the aromatic nucleus with the main chain of the polymer, and a method wherein an aromatic monovinyl polymer is treated with a Lewis acid in a solvent capable of forming a complex with the Lewis acid thereby to crosslink the polymer. However, these crosslinking methods require a long treatment time up to several days. For example, according to the latter method, in order to obtain insolubilized fibers of polystyrene having about 93% insolubility in toluene, an equilibrium swelling ratio of not more than 2.6 on a weight basis, and a resistance to shrinkage at a temperature up to 200° C., it is necessary to employ a commercially unsuitable process which involves immersing the fibers in a nitromethane solution of aluminium chloride at 30° C. for 24 hours. In the former method, fibers prepared from a blend of 85 parts of polystyrene and 15 parts of polybutadiene are immersed in 95% sulfuric acid at 25° C. for one day in order to cross-link them to such an extent that the fibers are endurable to dry cleaning and have resistance to shrinkage at a temperature up to 200° C.

In contrast, according to the present invention, when a fibrous material of polystyrene is immersed in chlorosulfonic acid at room

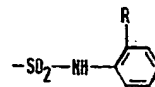
temperature for only 20 seconds, the fibrous material becomes solvent resistant. Thus, even if the fibrous material is heated under reflux in a solvent such as methylene chloride, trichloroethylene, benzene, toluene, tetrahydrofuran or N,N-dimethyl formamide, no decrease in weight is observed. The cross-linked fibrous material has an equilibrium swelling ratio in toluene of not more than 1.6, and a shrinkage of not more than 1.5% after standing in air at 200° C. for 1 hour and not more than 3% after standing in air at 250° C. for 1 hour. Thus, an insoluble infusible fibrous material having high levels of solvent resistance and thermal resistance can be obtained. Furthermore, the introduction of a metal-chelating group such as an amino group can be performed generally within 30 minutes to 5 hours. The process of this invention thus has commercial advantages.

The cross-linked filamentary structure is reacted in accordance with this invention with a reagent for introducing a metal-chelating group, thereby to introduce the metal-chelating group into at least some of the uncross-linked aromatic nuclear structural units.

Examples of the metal-chelating group are

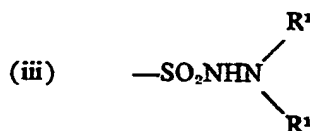


wherein n is an integer of 1 to 5;

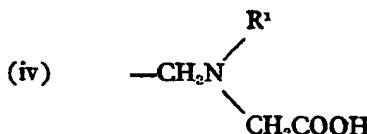


(ii)

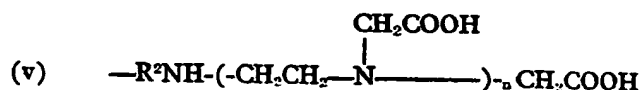
wherein R represents $-\text{OH}$, $-\text{SH}$, $-\text{NH}_2$, $-\text{CHO}$ or $-\text{COOH}$;



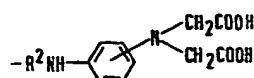
wherein each R^1 , which may be the same or different represents $-\text{H}$, an alkyl group containing 1 to 4 carbon atoms, a phenyl group or $-\text{CH}_2\text{COOH}$;



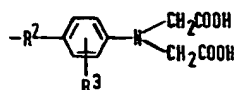
wherein R^1 is as defined for formula (iii);



wherein R^2 represents $-\text{CH}_2-$ or $-\text{SO}_2-$, and n is an integer of 1 to 5;

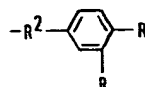


(vi)

wherein R² is as defined for formula (v);

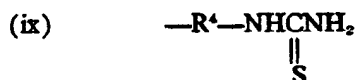
(vii)

- 5 wherein R² is as defined for formula (v) and R³ represents ---H , ---OH , ---SH or $\text{---N}(\text{CH}_2\text{COOH})_2$;

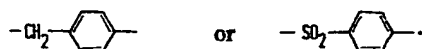


(viii)

- 10 wherein R² is as defined for formula (v) and each R which may be the same or different, is as defined for formula (ii); and



wherein R⁴ represents $\text{---CH}_2\text{---}$, $\text{---SO}_2\text{---}$, $\text{---CH}_2\text{NH---}$, $\text{---SO}_2\text{NH---}$,



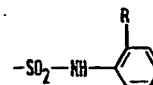
- 15 The means for introducing these metal-chelating groups into at least some of the uncrosslinked aromatic nuclear structural units in step b) may be carried out by any desired known reaction. Some preferred embodiments will be described below.

- 20 (1) The cross-linked filamentary structure is treated with a chlorosulfonating agent such as chlorosulfonic acid, then the treated structure is reacted with an amine having metal-chelating ability. Alternatively, it is possible to perform step a), the cross-linking reaction, with chlorosulfonic acid for a time longer than that required for the desired cross-linking, thereby to induce both the crosslinking and chlorosulfonation at the same time, and then reacting the filamentary structure with an amine having metal-chelating ability to convert the chlorosulfonyl groups to metal-chelating groups. According to this embodiment, the

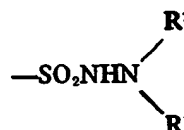
chlorosulfonyl groups can be converted to a metal-chelating group which is



wherein n is an integer of 1 to 5;



wherein R represents ---OH , ---SH , ---NH_2 , ---CHO or ---COOH ; or



wherein each R¹ which may be the same or different represents ---H , an alkyl group containing 1 to 4 carbon atoms, a phenyl group or $\text{---CH}_2\text{COOH}$.

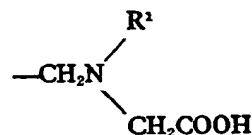
Examples of the amine are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, anthranilic acid, ortho-aminophenol, ortho-aminothiophenol, ortho-phenylene diamine, hydrazine, N-methylhydrazine, N-phenyl hydrazine, and N,N-dimethyl hydrazine.

More specifically, the following procedures are possible.

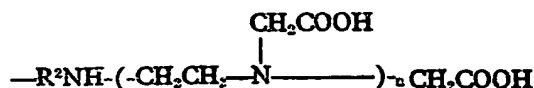
The cross-linking reaction is performed with chlorosulfonic acid having a concentration of more than 85% by weight, preferably more than 95% by weight, at -10 to 35°C ., preferably at 0 to 30°C . for a period of 30 seconds to 60 minutes, preferably 60 seconds to 30 minutes, and then reacted with one of the above amines.

(2) The cross-linked filamentary structure is chlorosulfonated or chloromethylated, and then reacted with an amine, after which the amino group and/or imino group introduced is carboxymethylated to impart metal chelating ability to the material.

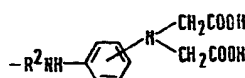
According to this embodiment, the following metal-chelating groups may be introduced



wherein R¹ represents ---H , an alkyl group containing 1 to 4 carbon atoms, a phenyl group or $\text{---CH}_2\text{COOH}$;



wherein R represents $-\text{CH}_2-$ or $-\text{SO}_2-$,
and n is an integer of 1 to 5; or



5 wherein R^2 is as defined above.

Examples of the chloromethylating agent which may be used are chloroalkyl ethers such as chloromethyl methyl ether, chloromethyl-ethyl ether or dichlorodimethyl ether; compounds capable of generating formaldehyde such as formaldehyde, para-aldehyde or trioxane; and dialkyl formals such as dimethyl formal or diethyl formal. These compounds may be used alone or in admixture of two or more. The chloromethylation using such a chloromethylating agent does not particularly require a catalyst, but usually, it is preferred to carry it out in the presence of an acid catalyst. Examples of such a catalyst are Lewis acids such as aluminum chloride, zinc chloride, stannic chloride or boron trifluoride/ether complex, or Brønsted acids such as sulfuric acid, hydrochloric acid, phosphoric acid or glacial acetic acid. The amount of the acid catalyst is, for example, 0.1 to 20 mols, preferably about 0.5 to 5 mols per mol of the chloromethylating agent.

The chloromethylated filamentary structure can then be reacted with ammonia and/or an amine, and then carboxymethylated to impart chelate-forming ability. The amine to be reacted with the chloromethylated filamentary structure may be a monoamine or a polyamine. Only polyamines may be used in this embodiment for a chlorosulfonated filamentary structure. Examples of the monoamines are methylamine, ethylamine, propylamine, aniline, glycine and alanine. Examples of the polyamines that can be reacted with the chloromethylated and chlorosulfonated filamentary structure are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and phenylene diamines. Desirably, the reaction with the amine is carried out by immersing the chloromethylated or chlorosulfonated filamentary structure in the undiluted amine or its solution. The reaction conditions differ according to the reaction reagent and solvent used. Generally, however, the reaction can be carried out under mild conditions, that is, at a temperature of 0 to 80° C. for 1 minute to 2 hours.

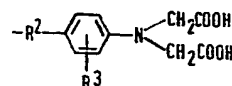
The carboxymethylating reaction can be carried out, for example, by a method wherein a halogenated acetic acid such as monochloro-

acetic acid, bromoacetic acid or iodoacetic acid is used as a reaction reagent, a method wherein the fibrous material is reacted with prussic acid or its salt and formaldehyde to carboxymethylate the material through a cyanomethyl group, a method wherein an epoxy compound such as ethylene oxide or propylene oxide or a halohydrin compound such as ethylene chlorohydrin is reacted with the amino group and/or imino group, followed by oxidation under mild conditions, or a method wherein the amino and/or imino group are reacted with an amino acid such as glycine or alanine to perform an amine exchange reaction and carboxymethylate the fibrous material.

Of these methods, the method using the halogenated acetic acid is especially preferred. In this method, the carboxymethylating reaction is carried out in an aqueous solution of an alkali metal salt of a halogenated acetic acid at 10 to 150° C., preferably 60 to 120° C. for 10 minutes to 3 hours, preferably 30 minutes to 2 hours. The amount of the halogenated acetic acid is desirably 2 to 100 equivalents per equivalent of the amino group introduced into the fibrous material in view of the amount to be lost by hydrolysis during the reaction.

(3) The above-mentioned cross-linked and chlorosulfonated or chloromethylated filamentary structure is reacted with an aromatic amine in the presence of an acid catalyst. By subjecting the filamentary structure to the above Friedel-Crafts reaction, the aromatic nucleus of the structural unit derived from an aromatic monovinyl monomer is substituted by the aromatic amine group. Then, the aromatic amine group introduced is carboxymethylated to convert it to a metal-chelating group.

According to this embodiment, the following metal-chelating groups may be introduced:



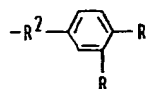
wherein R^2 represents $-\text{CH}_2-$ or $-\text{SO}_2-$, and R^3 represents $-\text{H}$, $-\text{OH}$, $-\text{SH}$ or $-\text{N}(\text{CH}_2\text{COOH})_2$. Examples of the aromatic amine are *o*-aminophenol, *o*-aminothiophenol, and *o*-phenylene diamine.

Examples of the acid catalyst described above are Lewis acids such as aluminum chloride, zinc chloride, or boron trifluoride-ether complex, and Brønsted acids such as sulfuric acid, phosphoric acid or glacial acetic acid.

The reaction with the aromatic amine can be performed by immersing the chlorosulfonated or chloromethylated fibrous material in a solution containing the aromatic amine compound and acid catalyst, and allowing it to react at 30 to 100° C. for 10 minutes to 2 hours. In this case, the amino and/or imino group forms a quaternary salt with the acid catalyst, and therefore does not form a sulfonamide group or aminomethyl group by reaction with a chlorosulfonyl group or chloromethyl group. Accordingly, in view of the amount to be lost by the formation of the quaternary salt with the amino and/or imino group the amount of the acid catalyst should be in excess of the amount of the aromatic amine. Where a Brønsted acid is used as a catalyst, it can be used in large excess in order to make it act concurrently as a solvent.

The carboxymethylating agent and carboxymethylation are the same as those described in (2) above.

(4) The above-mentioned cross-linked and chlorosulfonated or chloromethylated filamentary structure is reacted in the presence of an acid catalyst with an aromatic compound having metal chelating ability. By this Friedel-Crafts reaction, the chlorosulfonyl or chloromethyl group can be converted to a metal-chelating group of the formula

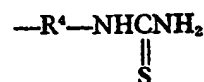


wherein R² represents $\text{---CH}_2\text{---}$ or $\text{---SO}_2\text{---}$ and each R, which may be the same or different, represents ---OH , ---SH , ---NH_2 , ---CHO or ---COOH .

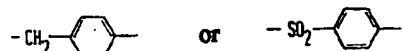
Examples of the above aromatic compound having metal-chelating ability are anthranilic acid, *o*-aminophenol, *o*-aminothiophenol, *o*-phenylene diamine, *o*-phenylene diamine tetraacetic acid, aniline diacetic acid, salicylic acid, thiosalicylic acid, salicylaldehyde, salicylaldoxime, catechol, alpha - benzyldioxime, alpha-furyl dioxime, 2,2'-dipyridyl, 1,10-phenanthroline, diphenylcarbazide, diphenyl carbazone, phenolphthalein, oxine, thioxine, alpha-benzoinoxime, quinaldinic acid, alpha-nitroso-beta-naphthol, 1-pyridyl azo-2-naphthol, N-benzoyl phenyl hydroxylamine, thenoyl trifluoroacetone, fruoyl trifluoroacetone, phenyl fluorone, alizarin, quinalizarin, resorcinol acid, *p*-aminosalicylic acid, 2-hydroxy-1-naphthaldehyde, 3-phenylhydroxy thiourea, diphenyl

thiocarbodiazone, toluene-3,4-dithiol, 2-mercaptobenzothiazole, and benzyl mercaptan. The acid catalyst may be one of those listed in (3) above.

(5) According to this embodiment the above-mentioned cross-linked and chlorosulfonated or chloromethylated filamentary structure is reacted with ammonia and/or an amine, and then the amino group-introduced structure is reacted with a thiocyanate salt. When an aromatic amine is used as said amine compound, the reaction is carried out in the presence of an acid catalyst. According to this embodiment, the chlorosulfonated group can be converted to a metal-chelating group of the formula



wherein R⁴ represents $\text{---CH}_2\text{---}$, $\text{---SO}_2\text{---}$, $\text{---CH}_2\text{NH---}$, $\text{---SO}_2\text{NH---}$,

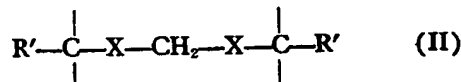


Examples of the amine are methylamine, ethylamine, ethylene diamine, diethylene triamine, aniline and hydrazine. The acid catalyst to be used when the amine compound is an aromatic amine may be one of those listed in (3) above.

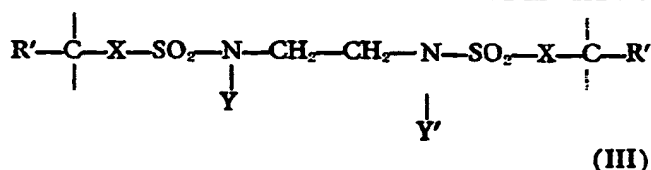
The thiocyanate salt may be any that is water-soluble. Preferred examples are ammonium, sodium or potassium salt of thiocyanic acid. The reaction with ammonia and/or an amine can be performed in the same way as in the reaction with ammonia and/or amine compound described in paragraph (2) above.

The reaction with the thiocyanate salt can be carried out at a temperature of 60 to 100° C. for 5 minutes to 2 hours.

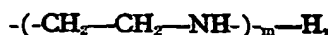
According to this invention, when the metal-chelating group-introducing reaction is performed, a crosslinked component expressed by the following formulae (II) to (IV) may be formed in a minor amount as a result of a side reaction:



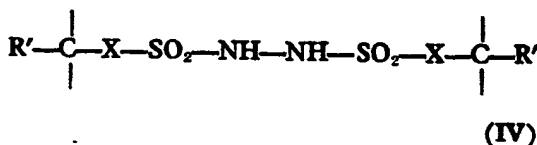
wherein each X and each R' are as defined for formula (I),



wherein each of Y and Y' which may be the same or different, represent the formula



in which m for Y and for Y' are each zero or an integer of 1 to 4 with the proviso that the sum of both m's is no more than 4, and each X and each R' are as defined for formula (I),



wherein each X and each R' are as defined for formula (I).

Accordingly, the metal-chelating, solvent-resistant filamentary structure obtained in accordance with this invention can have 2 to 40 per 100 of its aromatic nuclear structural units cross-linked to provide cross-linked components of formula (I) alone, or of formula (I) and of formula (II), (III) or (IV).

The filamentary structure of this invention can form metal-chelates with various metal ions. Such metal ions are, for example, ions of copper, mercury, cadmium, lead, nickel, iron, cobalt, zinc, manganese, calcium, barium, silver, and other heavy metals.

The filamentary structure of this invention is sparingly soluble in a solvent for polystyrene, and scarcely undergoes any chemical change such as hydrolysis even under severe chemical conditions. Furthermore, it is scarcely deteriorated by the metal-chelate forming treatment or regeneration treatment. Accordingly, the filamentary structure of this invention proves useful in fields where ordinary metal-chelating filamentary structures are used, and for removing metal-ions or recovering useful metal-ions from aqueous solutions.

The invention will be illustrated more specifically by the following Examples in which all parts and percentages are by weight. The "metal-chelating capacity" and "rate of crosslinking" were measured and determined as described below.

Metal-chelating capacity.

A sample of the metal-chelating filamentary structure (1 g) is immersed at room temperature for 5 hours in 100 ml. of an aqueous solution containing 0.05 mol/liter of one kind of metal ions (for example, as regards copper ions, an aqueous solution containing 0.05 mol/liter of copper sulfate). Then, the concentra-

tion of the metal ions remaining in the solution is determined by an atomic absorbance method based on JIS K-0102. The difference between the concentration of the metal ions in the aqueous solution before the testing and that after the testing is determined.

Rate of crosslinking.

The rate (percent) of crosslinking with chlorosulfonic acid was calculated on the basis of the following equation, assuming that the increase in weight owing to the crosslinked sulfone group is obtained by subtracting Y, which is the weight increase owing to the chlorosulfonyl groups as measured from the chlorine analysis value, from X which is the total weight increase owing to the treatment with chlorosulfonic acid.

$$\text{Rate of crosslinking (\%)} = \frac{2 \times \left(\frac{\text{X} - \text{Y}}{62} \right) \times 100}{\text{Mols of the aromatic mono-vinyl compound in the fibrous structure}}$$

Incidentally, the rate of crosslinking (%) to provide components of formula (II) is a value conjectured from the value reported in literature and those of the formulae (III) and (IV) are calculated from the elemental analysis values.

The rate of crosslinking as obtained by this equation is defined as corresponding to the number of crosslinked components. For example, the rate of crosslinking of 10% means that 10 crosslinked components are provided per 100 of the aromatic nuclear structural units.

Example 1.

Nitrogen gas was introduced under a pressure of 15 Kg/cm² into molten polystyrene at a temperature of about 250° C. in an extruder, and it was thoroughly kneaded. The mixture was extruded from a die through a slit with a clearance of 0.225 mm and a width of 150 mm, and at the die exit, cooling air of about 20° C. was blown against the extruded, molten polymer mixture. Thus the extrudate was quenched to 55° C. and then withdrawn at a draft ratio of 150 and wound up. Then, 40 such wound-up sheets were laminated, opened in the transverse direction at an opening ratio of 10 times, and integrated by passing through, a roller press with a pressure of 40 kg/cm². Thus a sheet-like fibrous material having a reticulate fibrous structure was obtained.

The resulting fibrous material was dipped in chlorosulfonic acid at 25° C. for 20 seconds. It was then immersed in a 30% solution of chlorosulfonic acid in chloroform at 20° C. for 15 minutes, and then washed well in chloroform. Then, it was dipped in methanol to decompose and remove the unreacted chlorosulfonic acid.

The cross-linked and chlorosulfonated fibrous material thus obtained was then immersed in ethylene diamine at room temperature (about 25° C.) for about 30 minutes. Then, the fibrous material was washed well with water, and reacted with sodium monochloroacetate in the form of a 20% aqueous solution at 80 to 90° C. for 1 hour. The resulting fibrous material was washed with water and dried. The metal-chelating capacity and other properties of the resulting fibrous material having an ethylene diamine-N,N-diacetic acid group are shown in Table I to be given later on.

When the fibrous material which captured metal ions as a chelate was treated with 1N hydrochloric acid at 25° C., the metal ions could be dissolved and the fibrous material could be repeatedly used. Even after repeating the metal ion capturing and the regeneration treatment 10 times, no deterioration in the properties of the fibrous material could be seen.

Example 2.

A polystyrene reticulate fibrous material obtained in the same way as in Example 1 was immersed for 5 seconds in chlorosulfonic acid at 20° C., and chlorosulfonic acid remaining in methanol was completely decomposed and removed. The fibrous material was then washed with methanol, and dried. The material was then immersed for 30 minutes at 20° C. in a solution consisting of 40 parts of petroleum ether, 30 parts of chloromethyl methyl ether and 30 parts of stannic chloride, to chloromethylate the fibrous material. After

the completion of the reaction, the fibrous material was washed with petroleum ether, and then immersed in methanol to decompose and remove the stannic chloride remaining therein, followed by drying. The chloromethylated polystyrene non-woven fabric was reacted with ethylene diamine at 70° C. for 30 minutes, and well washed with water. Then, it was further reacted for 1 hour at 80 to 90° C. in a 20% aqueous solution of sodium monochloroacetate to form a fibrous material having an iminoacetic acid group. The properties of the fibrous material are shown in Table I.

Example 3.

A polystyrene reticulate fibrous material obtained in the same way as in Example 1 was immersed for 10 seconds in chlorosulfonic acid at 20° C., and then transferred to a 30% chloroform solution of chlorosulfonic acid. The fibrous material was allowed to react therein for 15 minutes at 20° C. After the end of the reaction, it was washed with chloroform to remove the remaining unreacted chlorosulfonic acid sufficiently. Then, the fibrous material was dipped in methanol to decompose and remove the chlorosulfonic acid completely. The chlorosulfonated polystyrene fibrous material was dipped for 30 minutes in a 20% acetic acid solution of catechol at 90° C. to form a chelate-forming fibrous material having a 3,4-dihydroxyphenyl-sulfone group. The properties of the resulting fibrous material are shown in Table I below.

Example 4.

A sheet-like fibrous material composed of 80 parts of polystyrene and 20 parts of polyethylene produced in the same way as in Example 1 was dipped for 10 seconds in chlorosulfonic acid at 20° C., and then transferred to a 30% chloroform solution of chlorosulfonic acid. Then, it was reacted for 15 minutes at 20° C. After the end of the reaction, the remaining unreacted chlorosulfonic acid was washed off in chloroform to decompose and remove a tiny amount of the chlorosulfonic acid completely. The chlorosulfonated fibrous material was dipped for 30 minutes in a 30% acetic acid solution of thiophenol at 90° C. to form a chelate-forming fibrous material having a 4-mercaptophenyl sulfone group. The properties of this fibrous material are shown in Table I.

Example 5.

A polystyrene reticulate fibrous material produced in the same way as in Example 1 was squeezed at 20° C. and then treated with methanol to decompose and remove the remaining chlorosulfonic acid completely. It was then washed with methanol, and dried whereby a crosslinkage occurred at a rate of

13.0% of the aromatic ring contained in the polymer molecule to render the fibrous material insoluble in solvent. The cross-linked infusible fibrous material was dipped in a 30% chloroform solution of chlorosulfonic acid, and allowed to react therein for 15 minutes at 20° C. After the end of the reaction, the unreacted chlorosulfonic acid was completely decomposed and removed in chloroform. The chlorosulfonated polystyrene fibrous material was dipped for 30 minutes in a 20% acetic acid solution of aniline at 90° C. to form a polystyrene fibrous material having a *p*-sulfonyl aniline group. The fibrous material was treated with a 10% aqueous solution of sodium hydroxide, and then dipped in a 20% aqueous solution of sodium monochloroacetate, followed by allowing it to react for 1 hour at 90° C. to carboxymethylate the amino groups. After the end of the reaction, the product was washed with water and dried to form a chelate-forming fibrous material having a *p*-sulfonyl aniline-*N,N*-diacetic acid group. The properties of the resulting fibrous material are shown in Table I.

The fibrous material having chelate-forming ability completely retained the form of the original fibrous material before the above chemical treatment. It had sufficient flexibility, and scarcely swelled when immersed in water. This fibrous material was repeatedly used 10 times in a copper ion capturing reaction using a 0.1 M copper sulfate aqueous solution and regenerated 10 times using 1N hydrochloric acid. The strength of the fibrous material and its metal ion-capturing ability were not changed, but exhibited superior chemical resistance.

Example 6.

A polystyrene reticulate fibrous material produced in the same way as in Example 1 was dipped for 10 seconds in chlorosulfonic acid at 20° C., and squeezed well in methanol to decompose and remove the chlorosulfonic acid completely. Then, the fibrous material was washed with methanol and washed whereby a crosslinkage occurred at a rate of 12.5% of the aromatic rings contained in the polymer molecules, and the fibrous material was rendered insoluble in solvent. This crosslinked insoluble fibrous material was dipped in a 30% chloroform solution of chlorosulfonic acid, and allowed to react for 15 minutes at 20° C. After the end of the reaction, the remaining unreacted chlorosulfonic acid was thoroughly washed off in chloroform, and then the fibrous material was dipped in methanol to decompose and remove a tiny amount of the remaining chlorosulfonic acid completely. The chlorosulfonated polystyrene fibrous material was dipped in ethylene diamine at 20° C. and allowed to react for 30 minutes. Then, the fibrous material was thoroughly

washed with water and dried to form a chelate-forming fibrous material having an *N*-(beta-aminocethyl, sulfonamide group. The properties of the resulting fibrous material are shown in Table I.

This chelate-forming fibrous material completely retained the form of the original material before the chemical treatment. It had sufficient flexibility and was scarcely swelled even when immersed in water. When this fibrous material was repeatedly used 10 times in a copper ion capturing reaction using 0.1M ammonia-basic copper sulfate aqueous solution and the desorption with 1N hydrochloric acid and the regeneration with 1N aqueous solution of sodium hydroxide, the strength of the fibrous material and the metal ion capturing capacity scarcely changed. It was confirmed that the fibrous material so treated had good chemical resistance.

Example 7.

A fibrous material composed of 90 parts of polystyrene and 10 parts of polypropylene produced in the same way as in Example 1 was dipped in chlorosulfonic acid at 25° C., and then well squeezed. The unreacted chlorosulfonic acid was thoroughly washed off in methylene chloride. The fibrous material was then dipped in methanol to decompose and remove a tiny amount of the remaining chlorosulfonic acid completely. As a result of this chlorosulfonation, the rate of crosslinkage became 31.5%, and the degree of chlorosulfonation became 68.5%. The fibrous material was dipped in ethylene diamine at room temperature, and reacted for 30 minutes. Then, it was washed well with water, and then allowed to react for 1 hour at 80 to 90° C. in a 20% aqueous solution of sodium monochloroacetic acid. After the end of the reaction, it was well washed with water, and dried to form a chelate-forming fibrous material which had an ethylene diamine-*N,N*-diacetic acid structure, a copper ion adsorbing capacity of 1.28 millimols/g, and a mercuric ion adsorbing capacity of 1.40 millimols/g. By treating the fibrous material which had adsorbed metal ions with 1N of hydrochloric acid, the metal ions were dissolved out and the fibrous material could be used repeatedly. The properties of the fibrous material are shown in Table I.

Example 8.

A reticulate fibrous material composed of 90 parts of polystyrene and 100 parts of polypropylene produced in the same way as in Example 1 was dipped for 10 seconds in chlorosulfonic acid at 20° C., and then transferred to a 30% methylene chloride solution of chlorosulfonic acid. After the reaction, the remaining unreacted chlorosulfonic acid was thoroughly washed in methylene chloride. The

fibrous material was dipped in methanol to decompose and remove a tiny amount of the remaining chlorosulfonic acid completely. The chlorosulfonated fibrous material was immersed for 10 minutes at room temperature in 80% hydrazine hydrate, and then washed well with water. Then, it was heated under reflux for 1 hour in an aqueous solution containing 10% of thiocyanic acid and 7% of ammonia. After the end of the reaction, the fibrous material was washed well, and dried to form a chelate-forming fibrous material having a sulfonyl thiosemicarbazide structure. This fibrous material had a copper ion adsorbing capacity of 1.80 millimols/g, and no decrease in adsorbing capacity was observed at the time of desorption and regeneration with 1N hydrochloric acid. The properties of the fibrous material are shown in Table I.

20 Example 9.

A fibrous material having a sulfone hydrazide group as a chelate-forming group was produced in the same way as set forth in Example 8. The properties of the fibrous material are shown in Table I.

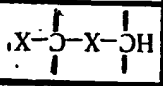
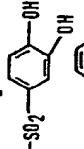
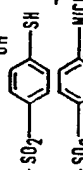
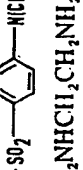
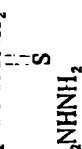
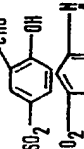
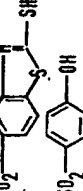
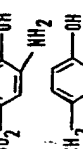
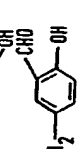

Examples 10 to 12.

A cross-linked and chlorosulfonated fibrous material produced in the same way as in Example 3 was dipped in a 20% acetic acid solution of salicylaldehyde, 2-mercaptobenzothiazole, and *o*-aminophenol respectively, and allowed to react for 30 minutes at 90° C. to form chelate-forming fibrous materials having a 3 - formyl - 4 - hydroxyphenyl sulfone group, 2-mercaptobenzothiazolyl sulfone group and 3 - amino - 4 - hydroxyphenyl sulfone group, respectively. The properties of these fibrous materials are shown in Table I.

Examples 13 and 14.

A crosslinked and chloromethylated fibrous material produced in the same way as in Example 2 was reacted for 1 hour at 90° C. in a 20% acetic acid solution of catechol and salicylaldehyde respectively to form chelate-forming fibrous materials having a 3,4-dihydroxybenzyl group and 3 - formyl - 4-hydroxybenzyl group, respectively. The properties of these fibrous material are shown in Table I.

TABLE I

Examples Nos.	Cross-linked structure				Metal-chelating groups	Properties				
	Number of cross-linkages of formula (I) (1)	Number of cross-linkages of formula (II) (1)		Number of cross-linkages of formula (III) & (IV) (1)		Chelating capacity (m. mol/g) (2)	Boiling toluene insoluble content (%) (3)	Equilibrium swelling ratio in toluene (4)	Shrinkage (%) after heating in air at 200°C for 1 hr. (5)	Time required for the reaction (min.) (6)
1	14.5	0	0	31.4	$-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$	1.28(Cu ^{II}) 1.49(Hg ^{II}) 1.54(Ag ⁺) 1.00(Cu ⁺)	0	1.2	0.7	105
2	9.8	#	0	20.8	$-\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$		0	1.6	1.0	120
3	11.6	0	0	0	CH_2COOH 	1.20(Cu ^{II})	0	1.5	1.0	45
4	11.6	0	0	0		1.20(Cu ^{II})	0	1.5	1.0	45
5	13.0	0	0	0	$-\text{SO}_2-\text{NCH}_2\text{COOH}_2$ 	0.82(Cu ^{II})	0	1.5	1.0	105
6	12.5	0	0	0	$-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	1.22(Cu ^{II})	0	1.5	1.0	45
7	31.5	0	0	14.0	$-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$	1.28(Cu ^{II}) 1.40(Hg ^{II}) 1.80(Cu ^{II})	0	1.1	0.5	100
8	11.3	0	0	25.2	$-\text{SO}_2\text{NHNHCNHS}$ 		0	1.5	1.0	85
9	12.8	0	0	24.6	$-\text{SO}_2\text{NHNH}_2$	2.48(Cu ^{II})	0	1.5	1.0	30
10	12.0	0	0	0		1.05(Cu ^{II})	0	1.5	1.0	45
11	11.3	0	0	0		1.20(Cu ^{II})	0	1.5	1.0	45
12	11.6	0	0	0		1.25(Cu ^{II})	0	1.5	1.0	45
13	9.8	0	0	0	$-\text{CH}_2-$ 	0.89(Cu ^{II})	0	1.5	1.0	90
14	9.5	#	0	0	$-\text{CH}_2-$ 	0.82(Cu ^{II})	0	1.6	1.0	90

Notes to Table I.

The items marked 1) to 6) in the above table have the following meanings.

1): Number of crosslinkages per 100 aromatic nuclear structural units.

2): In the parentheses after the numerical figures, metal ions are shown.

3): The polystyrene fibrous material was immersed for 24 hours in boiling toluene at atmospheric pressure, and then dried to a constant weight. The percentage of the weight of the treated fibrous material based on the weight of the material before treatment was measured.

4): The polystyrene fibrous material was immersed for 72 hours in toluene at room temperature, and toluene adhering to the surface of the material was wiped off well by a filter paper. The weight of the treated material was measured, and the ratio of it based on the weight of the original fibrous material before immersion in toluene was calculated.

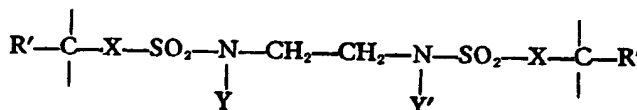
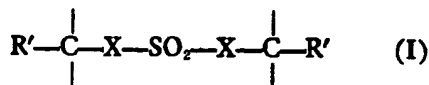
5): A 20 mm wide and 100 mm long polystyrene non-woven cloth was cut out in the direction of the fiber axis, and heated for 1 hour at 200° C. in air. The percentage of the change in length was calculated as against the original length before heating.

6): The total of the crosslinking reaction time and the metal-chelating group introducing time.

*The number of crosslinkages is not more than 2.

WHAT WE CLAIM IS:—

1. A metal-chelating, solvent-resistant, filamentary structure (as hereinbefore defined) comprising at least 20% by weight of aromatic nuclear structural units derived from an aromatic monovinyl monomers, which monomer may have a substituent in the ring or a methyl substituent in the α -position, 2 to 40 per 100 of the aromatic nuclear structural units being cross-linked via an $-\text{SO}_2-$ group to provide a cross-linked component of the following formula (I)

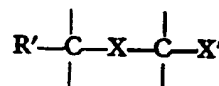


(III)

wherein each of Y and Y' which may be the same or different, represents the formula



wherein each X, which may be the same or different, represents one of said aromatic nuclear structural units, and each R', which may be the same or different, represents a hydrogen atom or a methyl group, the filamentary structure not containing a cross-linked component of the formula



wherein X' represents $-\text{H}$ or X and X and R' are as defined above, and at least some of the uncrosslinked aromatic nuclear structural units having a metal-chelating group incorporated therein.

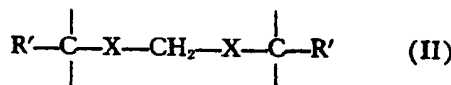
2. A filamentary structure according to claim 1 wherein the aromatic nuclear structural units are derived from one or more aromatic monovinyl monomers selected from styrene, α -methyl styrene, halogenated styrenes and vinyl naphthalenes.

3. A filamentary structure according to claim 1 or 2 comprising not more than 80% by weight of units derived from ethylene, propylene, acrylonitrile, vinyl acetate or methacrylic acid esters.

4. A filamentary structure according to claim 1, 2 or 3 comprising at least 40% by weight of said aromatic monovinyl nuclear structural units.

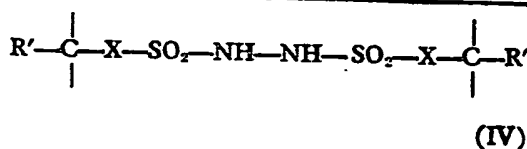
5. A filamentary structure according to any one of the preceding claims wherein 5 to 15 per 100 of the aromatic nuclear structural units are cross-linked via an $-\text{SO}_2-$ group to provide a cross-linked component of formula (I) in claim 1.

6. A filamentary structure according to any one of the preceding claims wherein 2 to 40 per 100 of the aromatic nuclear structural units are cross-linked to provide cross-linked components of formula (I) in claim 1 and of one or more of the following formulae (II), (III) and (IV),



wherein each X and each R' are as defined in claim 1,

in which m for Y and m for Y' are each zero or an integer of 1 to 4 with the proviso that the sum of both m's is no more than 4, and each X and each R' are as defined in claim 1, and



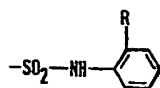
wherein each X and each R' are as defined in claim 1.

- 5 7. A filamentary structure according to any one of the preceding claims wherein the metal-chelating group is

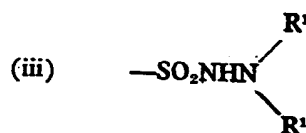


wherein n is an integer of 1 to 5;

(ii)

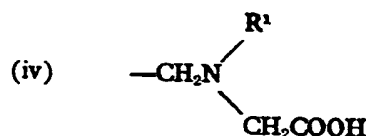


- 10 wherein R represents $-\text{OH}$, $-\text{SH}$, $-\text{NH}_2$, $-\text{CHO}$ or $-\text{COOH}$;

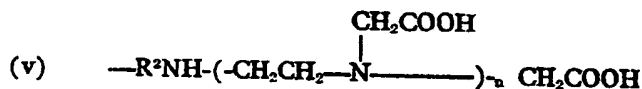


wherein each R¹, which may be the same or different, represents $-\text{H}$, an alkyl group containing 1 to 4 carbon atoms, a phenyl group or $-\text{CH}_2\text{COOH}$;

15

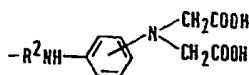


wherein R¹ is as defined for formula (iii);



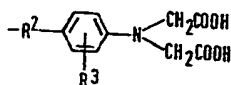
- 20 wherein R² represents $-\text{CH}_2\text{---}$ or $-\text{SO}_2\text{---}$, and n is an integer of 1 to 5;

(vi)



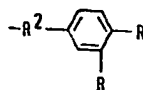
wherein R² is as defined in formula (v);

(vii)

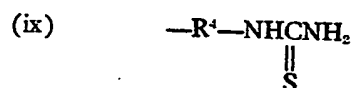


- 25 wherein R² is as defined for formula (v) and R³ represents $-\text{H}$, $-\text{OH}$, $-\text{SH}$ or $-\text{N}(\text{CH}_2\text{COOH})_2$;

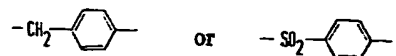
(viii)



- 30 wherein R² is as defined for formula (v) and each R which may be the same or different, is as defined for formula (ii); or



wherein R⁴ represents $-\text{CH}_2\text{---}$, $-\text{SO}_2\text{---}$, $-\text{CH}_2\text{NH---}$, $-\text{SO}_2\text{NH---}$,



35

8. A filamentary structure according to any one of the preceding claims which is insoluble in toluene at its boiling point under atmospheric pressure.

9. A filamentary structure according to any one of the preceding claims in the form of a non-woven fabric which is a polystyrene reticulate fibrous material.

40

10. A filamentary structure according to claim 1 substantially as hereinbefore described.

45

11. A filamentary structure as described in any one of the foregoing Examples.

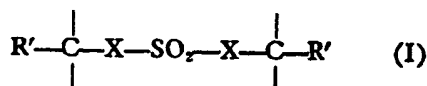
12. A method for producing a metal-chelating solvent-resistant filamentary structure (as hereinbefore defined), which method comprises

50

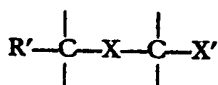
a) reacting a polymeric filamentary structure with chlorosulfonic acid, the polymer comprising at least 20% by weight of aromatic nuclear structural units derived from an aromatic monovinyl monomer,

55

- 5 which monomer may have a substituent in the ring or a methyl substituent in the α -position, to form a cross-linked polymeric filamentary structure in which 2 to 40 per 100 of the aromatic nuclear structural units are cross-linked via an $-\text{SO}_2-$ group to provide cross-linked components of the formula (I)



- 10 wherein each X, which may be the same or different, represents one of said aromatic nuclear structural units and each R', which may be the same or different, represents a hydrogen atom or a methyl group, and
15 which does not contain cross-linked components of the formula



- 20 wherein X' represents $-\text{H}$ or X and X and R' are as defined above, and
25 b) reacting the cross-linked polymeric filamentary structure obtained in step a) with at least one reagent to introduce a metal-chelating group into at least some of the uncrosslinked aromatic nuclear structural units.

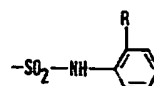
- 30 13. A method according to claim 12 wherein, in step b), the cross-linked polymeric filamentary structure is reacted with an aminating agent, a carboxymethylating agent, a thiocyanate salt or an aromatic compound having metal-chelating ability.

14. A method according to claim 12 or 13 wherein the metal-chelating group is



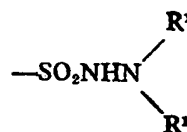
wherein n is an integer of 1 to 5;

(ii)

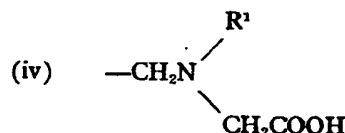


wherein R represents $-\text{OH}$, $-\text{SH}$, $-\text{NH}_2$, $-\text{CHO}$ or $-\text{COOH}$;

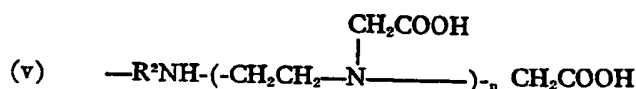
(iii)



wherein each R¹, which may be the same or different, represents $-\text{H}$, an alkyl group containing 1 to 4 carbon atoms, a phenyl group or $-\text{CH}_2\text{COOH}$;

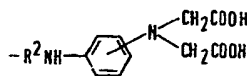


wherein R¹ is as defined for formula (iii);



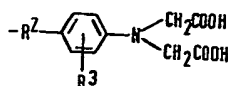
wherein R² represents $-\text{CH}_2-$ or $-\text{SO}_2-$, and n is an integer of 1 to 5;

(vi)



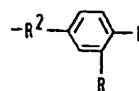
50 wherein R² is as defined for formula (v);

(vii)

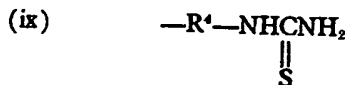


wherein R² is as defined for formula (v) and R³ represents $-\text{H}$, $-\text{OH}$, $-\text{SH}$ or $-\text{N}(\text{CH}_2\text{COOH})_2$;

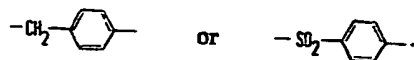
(viii)



wherein R² is as defined for formula (v) and each R which may be the same or different, is as defined for formula (ii); or



wherein R⁴ represents —CH₂—, —SO₂—,
—CH₂NH—, —SO₂NH—,



15. A method according to claim 12, 13
5 or 14 wherein, in step b), the cross-linked
polymeric filamentary structure is reacted with
any reagent specifically named herein for the
purpose.
16. A method according to claim 12 sub-
10 stantially as hereinbefore described.

17. A method substantially as described in
any one of the foregoing Examples.

18. A filamentary structure as claimed in
any one of claims 1 to 11 when produced
by a method as claimed in any one of claims
12 to 17. 15

19. A filamentary structure as claimed in
any one of claims 1 to 11 and 18 when
used to remove or recover metal ions from
aqueous solutions containing them. 20

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London, WC1R 5EU.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.